Source apportionment of sulfate and nitrate particulate matter in the Eastern United States and effectiveness of emission control programs

Hongliang Zhang [a,1], Jianlin Hu [b], Michael Kleeman [b], Qi Ying [a,*]

[a] Zachry Department of Civil Engineering, Texas A&M University, College Station, TX, USA
[b] Department of Civil and Environmental Engineering, University of California, Davis, CA, USA

HIGHLIGHTS

- Source contributions to secondary nitrate and sulfate in the eastern US were determined.
- Coal combustion and natural gas burning were major sources of sulfate.
- Vehicles, coal and natural gas burning were major sources of nitrate.
- Assessing the magnitude of control benefits needs to consider changes in meteorology.

ARTICLE INFO

ABSTRACT

Reducing population exposure to $PM_{2.5}$ in the eastern US will require control of secondary sulfate and nitrate. A source-oriented Community Multi-scale Air Quality (CMAQ) model is used to determine contributions of major emission sources to nitrate and sulfate concentrations in the seven eastern US cities (New York City, Pittsburgh, Baltimore, Chicago, Detroit, St. Paul, and Winston-Salem) in January and August of 2000 and 2006. Identified major nitrate sources include on-road gasoline-powered vehicles, diesel engines, natural gas and coal combustion. From 2000 to 2006, January nitrate concentrations decreased by 25–68% for all the seven cities. On average, ~53% of this change was caused by emissions controls while 47% was caused by meteorology variations. August nitrate concentrations decreased by a maximum of 68% in New York City but Detroit experienced increasing August nitrate concentrations by up to 33%. On average, ~33% of the reduction in nitrate is offset by increases associated with meteorological conditions that favor nitrate formation. Coal combustion and natural gas are the dominant sources for sulfate in both seasons. January sulfate decrease from 2000 to 2006 in all cities by 4–58% except New York City, which increases by 13%. On average, ~93% of the reduction in sulfate was attributed to emission controls with 7% associated with changes in meteorology. August sulfate concentrations decrease by 11–44% in all cities. On average, emission controls alone between 2000 and 2006 would have caused 6% more reduction but the effectiveness of the controls was mitigated by meteorology conditions more favorable to sulfate production in 2006 vs. 2000. The results of this study suggest that regional emissions controls between 2000 and 2006 have been effective at reducing population exposure to $PM_{2.5}$ in the eastern US, but yearly variations in meteorology must be carefully considered when assessing the exact magnitude of the control benefits.

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1. Introduction

Airborne particulate matter (PM) is a complex mixture of small particles and liquid droplets suspending in the atmosphere that can be emitted directly as primary PM or formed through gas-to-particle partitioning of semi-volatile products as secondary PM. In addition to its impacts on radiation balance and climate by directly absorbing and/or scattering incoming solar radiation (Charlson et al., 1992; Kiehl and Briegleb, 1993) and by indirectly acting as cloud condensation nuclei (CCN) (Cruz and Pandis, 1997; Jones et al., 1994), PM also adversely affects human health (Laden et al., 2006; Moolgavkar and Luebeck, 1996; Pope and Dockery, 2006; Schwartz et al., 2002) and thus life expectancy (Pope et al., 2009).

The eastern United States (US) experiences high PM concentrations by the North American standards (EPA, 2004). Based on the 2006 National Ambient Air Quality Standards (NAAQS) for 24-hour $PM_{2.5}$ mass concentration, 59 counties in 10 states in the eastern US are designated as non-attainment by the US Environmental

* Corresponding author. Tel.: +1 979 845 9709; fax: +1 979 862 1542.
E-mail address: qying@civil.tamu.edu (Q. Ying).
[1] Currently address: Department of Civil and Environmental Engineering, University of California, Davis, USA.

Protection Agency (EPA) (http://www.epa.gov/pmdesignations/2006standards/documents/finaltable2011.htm), and numerous epidemiological studies have related population health outcomes with particulate air pollution exposure in the eastern US (Bell et al., 2007; Dominici et al., 2006; Samet et al., 2000). Ammonium sulfate and nitrate are the major chemical components of PM in the eastern US, accounting for more than half of the PM$_{2.5}$ mass concentrations (EPA, 2004, 2012; Fine et al., 2008; Luo et al., 2011; Walker et al., 2012). Analyses of measurement data throughout the country reveal that particulate sulfate and nitrate have clear seasonal patterns. Sulfate (from SO$_2$ emissions) is more readily formed in the eastern US in summertime (July to September) while particulate nitrate (from NO$_x$ emissions) concentrations are higher in cooler weather. These trends reflect the balance between precursor emissions rates, chemical reaction rates, and equilibrium partitioning between the gas and condensed phases.

The relationship between secondary PM component concentrations and the emission rates of their primary precursors from different source categories needs to be studied in order to determine the contributions of different emission sources to secondary PM concentrations and adverse health effects, and to design more efficient emission control strategies. Different statistical and mechanistic methods have been developed for source apportionment studies. Statistical models such as chemical mass balance (CMB) and positive matrix factorization (PMF) are more useful for primary pollutants (Held et al., 2005; Norris et al., 2008). Sensitivity analysis methods such as Brute Force Method (BFM) and decoupled direct method (DDM) can be used to determine the relative importance of the emission from different sources, however, they are not able to quantify the total source contributions because the effects of local emissions perturbations cannot be accurately extrapolated in the non-linear chemical reaction system (Berglen et al., 2004; Liu et al., 2008). A rigorous approach that tracks the source contributions to both primary and secondary PM is the source-oriented external mixture (SOEM) method described by Mysliwiec and Kleeman (2002) and applied in 3D models (Ying and Kleeman, 2006; Zhang et al., 2014b). The SOEM method tracks gaseous precursor emissions from different source categories and their reaction products separately to retain source information. Particles are represented as external mixtures to determine contributions to primary PM. A simplified approach that utilizes source-oriented representation of gas phase emissions, chemical transformations and gas-to-particle partitioning of semi-volatile products but treats particles as internal mixtures has been implemented in the widely used Community Multi-scale Air Quality (CMAQ) model

developed by the US EPA. The expanded source-oriented CMAQ model has been applied to study source contributions to secondary PM in Texas (Zhang and Ying, 2011, 2012) and China (Wang et al., submitted for publication; Zhang et al., 2012). An alternative approach that determines the changes of the tracer concentrations at each time step using process analysis information and mass balance analysis instead of directly solving their concentrations based on the differential equations has also been proposed as a means to increase computation efficiency in source apportionment calculations (Wagstrom et al., 2008; Wang et al., 2009).

While a number of models are available for source apportionment of secondary PM$_{2.5}$ nitrate and sulfate, none of the models have been applied to extensively study the source contributions to sulfate and nitrate in the eastern US for periods long enough that include different meteorology and emission conditions. The objective of this study is to apply a source-oriented 3D regional chemical transport model to determine the source contributions of nitrate and sulfate in the eastern US with a focus on the seven urban areas in that region using four month-long PM modeling episodes, January and August of 2000 and 2006. The study also evaluates the importance of regional transport, changes in direct emissions and variations in meteorology conditions on PM$_{2.5}$ sulfate and nitrate concentrations in the eastern US.

2. Model description

In this study, a source-oriented version of the CMAQ model (based on CMAQ version 4.7.1) (Byun and Schere, 2006; Carlton et al., 2010) was applied to directly track precursors of sulfate and nitrate from various emission sources and determine their contributions to sulfate and nitrate concentrations. The detail of the source apportionment technique for secondary PM has been documented by Ying and Kleeman (2006) and its implementation in the CMAQ model has been reported in a previous publication (Zhang et al., 2012), thus only a short summary is provided here. The SAPRC-99 photochemical mechanism (Carter, 2000) was modified to include additional reactions and species so that NO$_x$ and SO$_2$ and their gas phase reaction products from different sources are separately tracked with source-tagged species. For example, model species SO2_X1 and SO2_X2 are used to represent SO$_2$ from two different sources. The current version of the modified SAPRC-99 mechanism with 304 gas phase species and 2000 gas phase reactions in the source-oriented CMAQ model can track up to 9 sources simultaneously in a single simulation. The SMVGEAR solver in the CMAQ distribution is
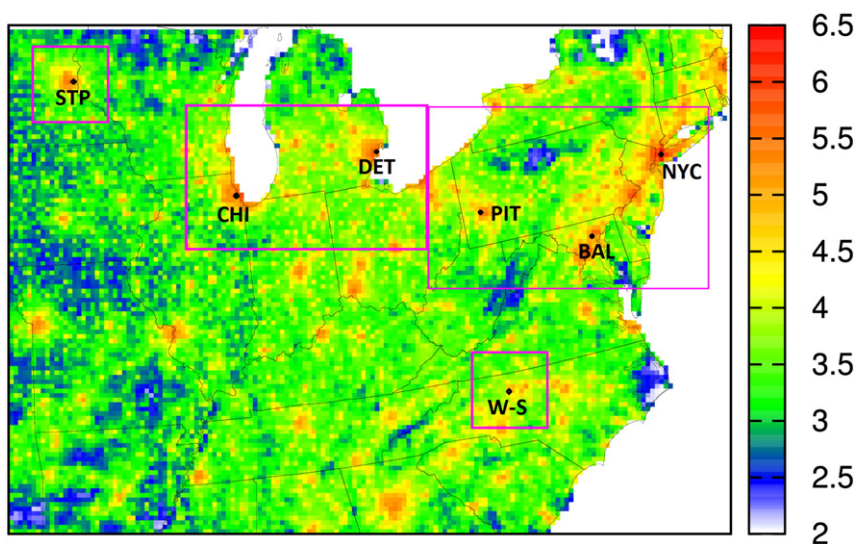

Fig. 1. The 12-km eastern US domain and the population density (per grid cell, in log-10 scale) in the area. The 36-km domain, which covers the entire continental US and part of Canada and Mexico, is not shown. The purple boxes are the nested 4-km domains.

Table 1

Emissions of NO_x and SO_2 from different source types within the 12-km eastern US domain on a typical weekday of January and August of 2000 and 2006. Units are kmol day^{-1}.

|		Jan. 2000	Jan. 2006	Aug. 2000	Aug. 2006
NO_x	Highway gasoline	169,915	133,727	126,686	116,955
	Off-highway gasoline	4276	4241	9781	8221
	Diesel engines	148,914	134,270	195,430	153,353
	Industries	27,500	19,721	30,468	21,286
	Natural gas	99,209	50,292	77,684	28,343
	Coal combustion	228,677	134,556	223,323	137,345
	Wildfire	2516	593	1423	2345
	Other	180,141	83,119	199,714	94,123
	Total	861148	560,519	864,509	561,971
SO_2	Highway gasoline	4274	1614	4264	2110
	Off-highway gasoline	129	44	243	84
	Diesel engines	4608	5125	8912	7885
	Industries	29,028	16,388	31,485	18,038
	Natural gas	51,575	1652	55,389	1917
	Coal combustion	414,430	355,980	423,779	358,196
	Wildfire	131	79	59	246
	Other	286,739	60,170	282,730	43,010
	Total	790,914	441,052	806,861	431,486

used to solve the time evolution of the gas phase species concentrations. The aerosol module AERO5 (Foley et al., 2010) was also modified to include additional source-tagged aerosol species and linked with the modified SAPRC-99 mechanism so that formation of secondary nitrate and sulfate from different sources through gas-to-particle partitioning, and heterogeneous and aqueous reactions can be correctly simulated within the AERO5 framework. The source-oriented CMAQ requires emissions of NO_x and SO_2 from different sources as separate input species, which can be prepared using a slightly modified Sparse Matrix

Operator Kernel Emission (SMOKE) model with user-supplied Source Classification Code lists as outlined by Ying and Krishnan (2010).

3. Model application

The source-oriented CMAQ model was applied to the eastern US to quantify the difference in source contributions to sulfate and nitrate between 2000 and 2006. For each year, a winter month (January) and a summer month (August) were simulated to represent formation of secondary inorganic compounds under different meteorology conditions. Three-level nested domains with horizontal resolutions of 36 km, 12 km, and 4 km, respectively, were used for the simulations. The 36-km domain with 160 × 124 grid cells covers the entire continental US and the 12-km domain with 159 × 111 grid cells covers the eastern US. Four 4-km domains are used to cover seven cities for detailed source apportionment analysis. The seven cities are: New York City (NYC), Pittsburgh (PIT), Baltimore (BAL), Chicago (CHI), Detroit (DET), St. Paul (S-P), and Winston-Salem (W-S). These seven cities are chosen because they mostly represent major metropolitan areas in the eastern US with relatively high PM loadings (NYC, PIT, BAL, CHI and DET) and have high population density (see Fig. 1). S-P and W-S are also metropolitan areas but with smaller population size. The 12-km eastern US domain, the nested 4-km domains and the locations of the seven cities are shown in Fig. 1.

Meteorological inputs used to drive the CMAQ simulations in this study were generated using the Weather Research and Forecasting (WRF) model v3.2.1. The 1° × 1° resolution NCEP (National Centers for Environmental Prediction) FNL (Final) Operational Global Analysis dataset (downloaded from http://rda.ucar.edu/dsszone/ds083.2/) was processed using the WRF Preprocessing System (WPS) to provide initial
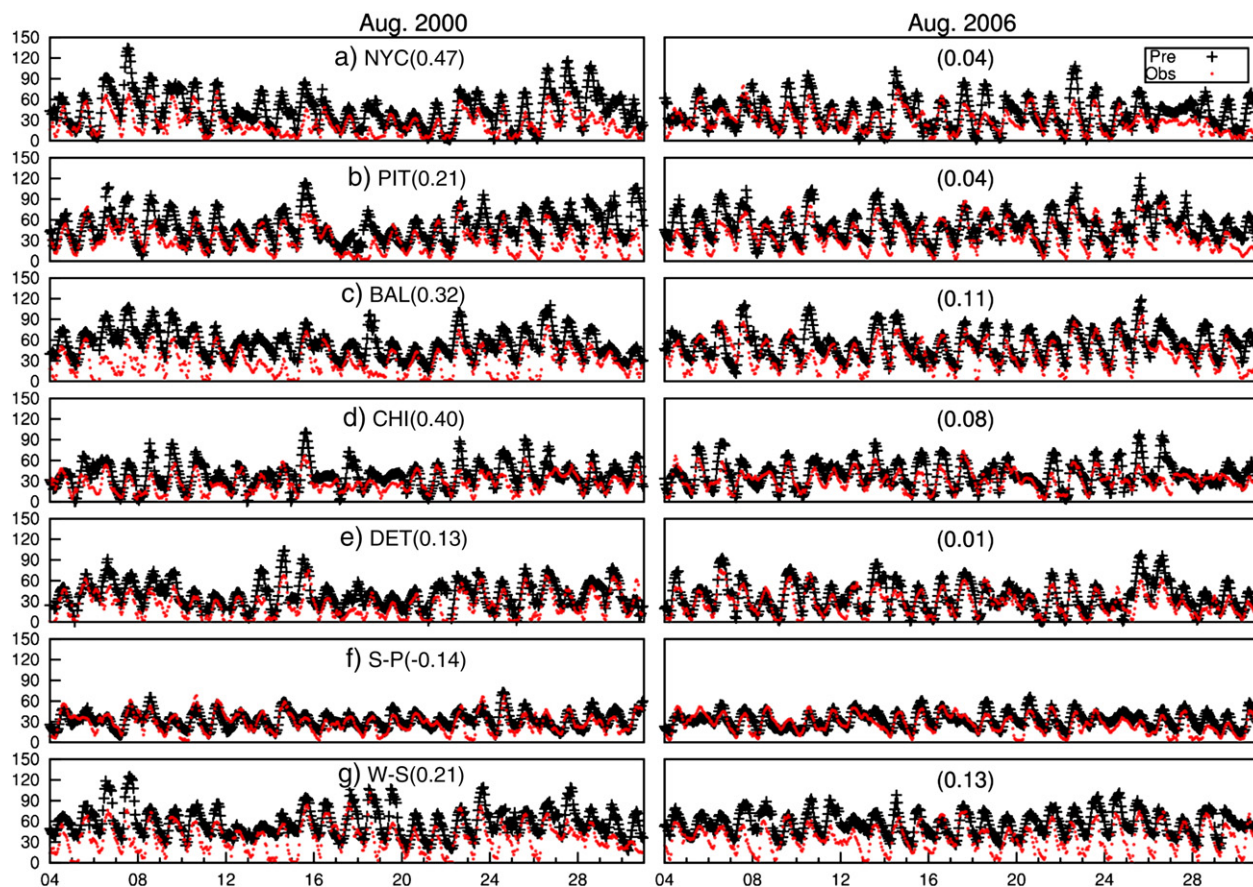
Fig. 2. Predicted and observed hourly O_3 concentrations in August 2000 and 2006. Units are ppb. Normalized mean bias (NMB) values are shown in parenthesis. A cut-off concentration of 60 ppb was applied in calculating NMB. There are no O_3 observations greater than 60 ppb at S-P for August 2006. NMB = $(1 / N)*\Sigma(P_i - O_i / O_i)$, where N is the total number of data points, P is prediction, O is observations and subscript i represents the ith data point. Numbers of available stations for NYC, PIT, BAL, CHI, DET, S-P, and W-S are 6, 3, 2, 9, 5, 9, and 3, respectively.

and boundary conditions for the WRF simulations. Two-way nested runs were conducted to simultaneously generate meteorological fields for the 36-km, 12-km and 4-km resolution domains. More details of the WRF model setup can be found in Zhang et al. (2014a).

The Sparse Matrix Operator Kernel Emissions (SMOKE) emission model (version 2.7) was used to process emissions for the CMAQ model. The 2001 Clean Air Interstate Rule (CAIR) emission inventory and the 2005 National Emission Inventory (NEI) version 2 were used to generate anthropogenic emissions for year 2000 and 2006, respectively. The Biogenic Emissions Inventory System (BEIS3.14) incorporated in SMOKE was used to generate biogenic emissions. Open biomass burning emissions for 2006 were based on an in-house tool that processes the satellite-observation based fire inventory from NCAR (Wiedinmyer et al., 2011). Additional details of the biomass burning processing can be found in Zhang et al. (2014a). Emissions from Canada and Mexico were also generated using the US EPA provided inventories (2005 for Canada and 2000 for Mexico). Modifications were made to the SMOKE model so that a Source Classification Code (SCC) list can be provided to generate emissions for a specific source category (Ying and Krishnan, 2010).

In this study, emissions of NO_x and SO_2 were split into seven different source types: highway gasoline vehicles, off-highway gasoline vehicles, diesel engines (including on-road diesel vehicles and off-road diesel powered equipment), industries, natural gas, coal combustion and wildfire. Sources that do not belong to these seven categories were lumped into the "other" source type. Major NO_x sources that were grouped into the 'other' source category include commercial fuel combustion, industrial equipment that uses liquefied petroleum gas,

commercial aircrafts and agriculture burning. Major SO_2 sources that were grouped into the 'other' source category include commercial marine vessels and industrial boilers using residual fuel and distillate oil. Table 1 shows the comparison of emissions of NO_x and SO_2 from different sources on a typical weekday for the four model months. Major emission sources for NO_x include highway gasoline, diesel engines, natural gas and coal combustion. NO_x emissions from all source types decreased from 2000 to 2006 except wildfires. Coal combustion is the dominating source for SO_2 followed by the "other" unresolved sources. Natural gas is the source with largest decrease of SO_2 from 2000 to 2006. Overall, for both January and August, NO_x emissions decreased by approximately 35% from 2000 to 2006 and SO_2 emissions decreased by approximately 45%.

The initial conditions for all domains and boundary conditions for the 36-km domain were generated using the default CMAQ profiles, which represent relatively clean continental conditions in the North America. Non-source-oriented simulations were conducted for the 36-km resolution US domain to provide boundary conditions for the 12-km resolution simulations. Source-oriented simulations were performed for 12-km and 4-km domains. Boundary conditions of NO_x, SO_2, nitrate and sulfate entering the 12-km domain, as determined by the non-source-oriented 36-km simulations, are tracked separately as "upwind sources" to differentiate them from the local source categories within the 12-km domain. The 4-km simulations use source-oriented boundary conditions which are determined based on the concentrations from the 12-km simulations. The first three days of each month were used as spin-up and are not used in subsequent analysis.
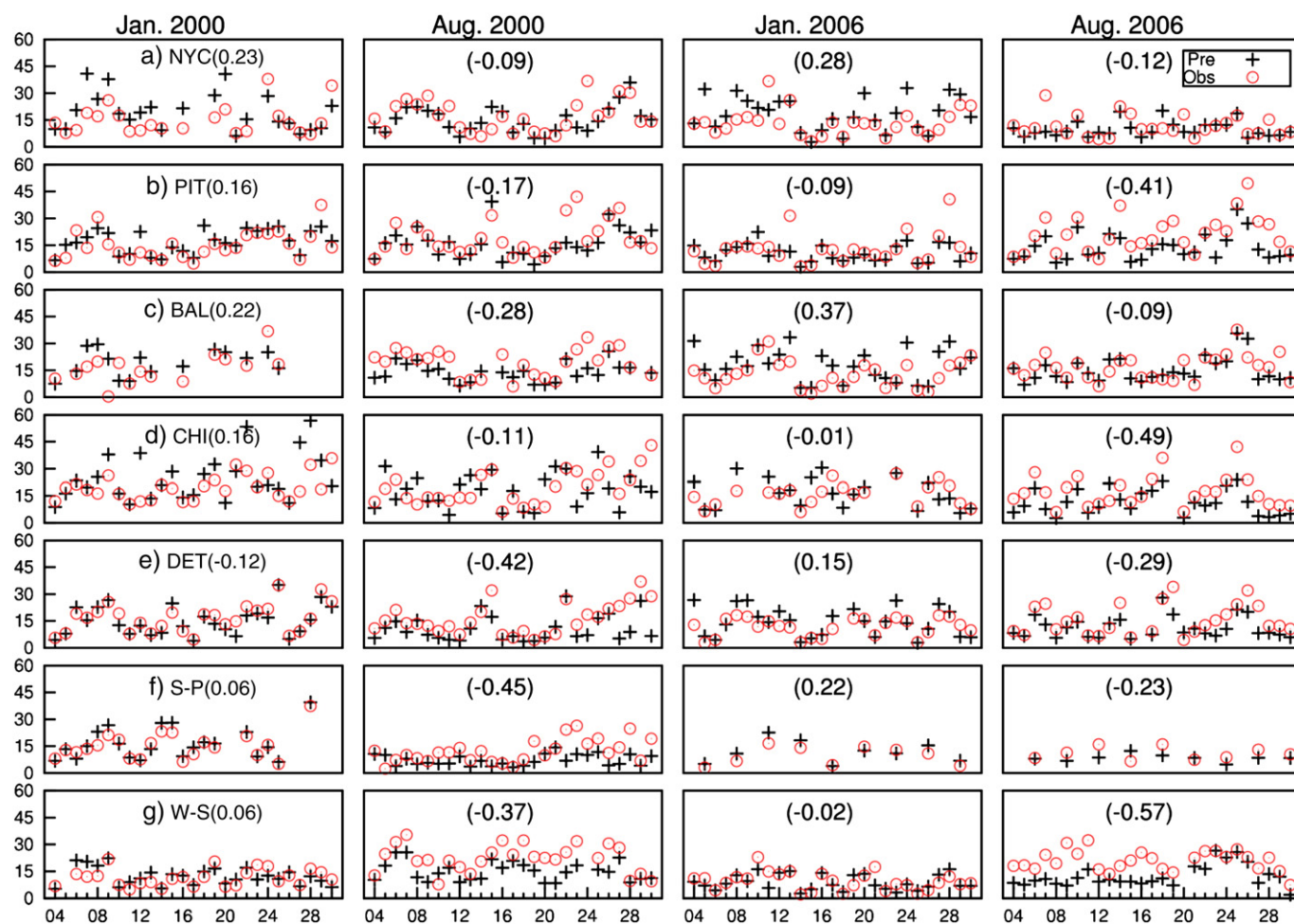

Fig. 3. Predicted and observed 24-hour average $PM_{2.5}$ concentrations in January and August of 2000 and 2006. Units are $\mu g\ m^{-3}$. Mean fractional bias (MFB) values are shown in parenthesis. $MFB = 2/N^*\Sigma(P_i - O_i) / (P_i + O_i)$. Numbers of available stations for NYC, PIT, BAL, CHI, DET, S-P, and W-S are 16, 10, 6, 9, 5, 4, and 2, respectively.

4. Results and discussion

4.1. Model performance

The evaluation of domain-wide meteorological and air quality model performance can be found in an accompany paper (Zhang et al., 2014a). Here we focus on the air quality model performance and source apportionment calculations based on the results from the 4-km domains for the seven cities of interest. A patch of 11 by 11 grid cells (44 by 44 km) surrounding each city center was used for all cities except W-S. A patch of 5 by 5 grid cells (20 by 20 km) was used for W-S to better match the size of this small city. Observations made at all stations within each city patch were averaged to represent concentrations for that city. Correspondingly, model predictions at the grid cells where the stations are located were also averaged and compared with the observations. All observations were downloaded from the Air Quality System (AQS) of US EPA (http://www.epa.gov/ttn/airs/airsaqs/detaildata/downloadaqsdata.htm).

Gas-phase chemical reactions oxidize SO_2 and NO_x into sulfate and nitrate. As a first check of gas-phase chemistry, it is necessary to evaluate the capability of the model to reproduce observed oxidant concentrations for species such as O_3. Fig. 2 shows the comparison of predicted and observed hourly O_3 concentrations along with the mean normalized bias (MNB) at the seven cities for August 2000 and 2006. High (>60 ppb) O_3 concentrations occurred in all cities except S-P. Generally, the model captures the diurnal variations and maximum concentrations of high O_3 events for all cities in both months. The model slightly over-predicts peak O_3 concentrations for most of the cities except S-P where the predictions agree well with the low observations. Over-prediction of nighttime O_3 can be observed for PIT, BAL and W-S (rows (b), (c) and (g)), which is likely due to an overestimation of vertical turbulent diffusion in the CMAQ model at night (Castellanos et al., 2011), causing O_3 from the mid atmosphere to mix to the surface level in model calculations.

Fig. 3 illustrates the comparison of predicted and observed 24-hour average $PM_{2.5}$ mass concentrations for all four months. In January 2000 (first column of Fig. 3), measurements and model predictions of $PM_{2.5}$ are generally in good agreement with MNB values in the range of −0.12 to 0.23. $PM_{2.5}$ concentrations are overestimated on some days of the month at NYC (11 days), PIT (3), BAL (5) and CHI (8), as can be seen from the positive MFB values. In August 2000 (second column of Fig. 3), measurements and model predictions are once again in good agreement with MFB ranging from −0.42 to −0.09. At DET (row (e)), the model fails to predict the persistent increase in $PM_{2.5}$ concentration during the last week of the month. At W-S (row (g)), concentrations are slightly under-predicted for the whole month. A comparison of predictions and observations for January 2006 is shown in the third column of Fig. 3. At S-P and W-S, model predictions agree well with observations. MFB values range from −0.09 to 0.37 for this month. $PM_{2.5}$ is both under-predicted and over-predicted at different times in NYC, PIT, BAL, CHI and DET, but the day-to-day variations are correctly captured. The last column of Fig. 3 shows the $PM_{2.5}$ predictions and observations in August 2006. The predicted $PM_{2.5}$ concentrations are generally lower than observations (MFB ranges from −0.41 to −0.09), except at W-S, where the under-prediction is more severe during the first half of the month (MFB = −0.57). Overall, the model simulations meet the EPA model performance criteria (MFB < 0.6) (U.S.EPA, 2007).

Fig. 4 shows the comparison of predicted and observed 24-hour average sulfate concentrations at the seven cities in January and August 2006. Observation data is not available for the year 2000. The observations in 2006 are available every three or six days. Generally the model predictions agree with observations although sulfate concentrations are under-predicted in the summer month especially for high concentration days. Larger MFB values in NYC (−0.54) and W-S (−0.57) are driven by one or two data points with significant differences. A
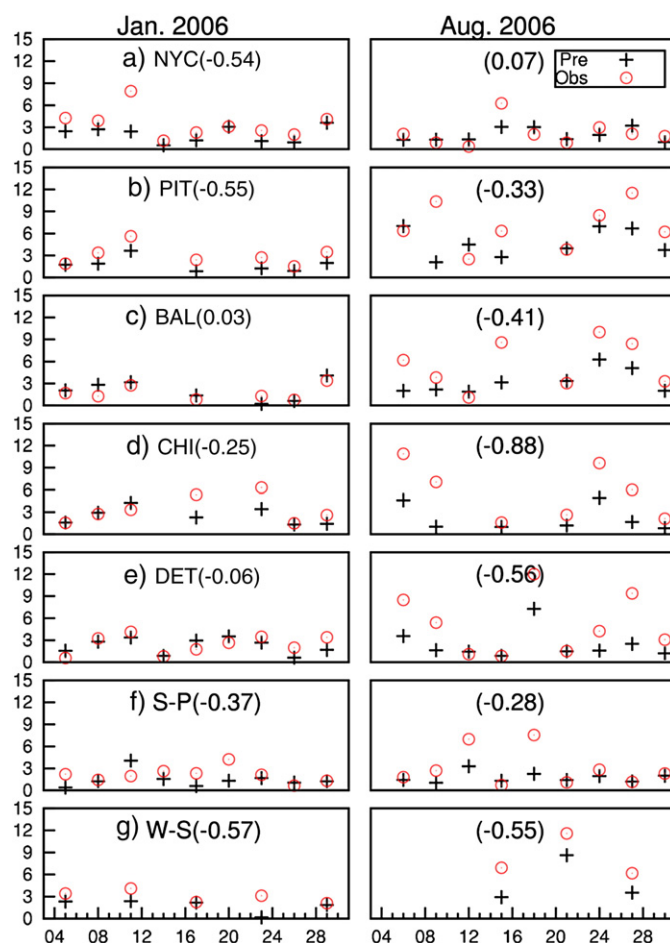

Fig. 4. Predicted and observed 24-hour average $PM_{2.5}$ sulfate at the seven cities in January and August of 2006. Each column represents one city. Units are μg m^{-3}. MFB values are shown in parenthesis. Numbers of available stations for NYC, PIT, BAL, CHI, DET, S-P, and W-S are 4, 2, 1, 2, 2, 2, and 1, respectively.

number of studies have noted sulfate under-predictions in CMAQ. For example, a seven-year CMAQ model study shows that sulfate is universally under-predicted in the eastern US in the summer months (Zhang et al., 2014a). Luo et al. (2011) attributed this under-prediction of sulfate to overestimation of wet scavenging by the CMAQ cloud module.

Based on the comparison with available observation data, the CMAQ model appears to be able to predict the concentrations and time-variation of O_3, $PM_{2.5}$ total mass, and sulfate. Although there are not enough observations in the study cities for a statistical evaluation of $PM_{2.5}$ nitrate, the domain-wide monthly concentrations have been shown to agree with available observations in Zhang et al. (2014a). Generally, the ability of the model to reasonably represent the major chemical, physical and transport processes governing pollutant concentrations increases confidence in the subsequent source apportionment analysis, although the uncertainties in the results are likely more significant at the sites with relatively poorer model performance.

4.2. Source apportionment of $PM_{2.5}$ nitrate and sulfate

Fig. 5 shows the monthly average nitrate concentrations at the seven cities in January and August 2000 and 2006 and the contributions of local and upwind sources to the predicted nitrate concentrations. First row shows the results in January 2000. The upwind sources emit precursor NO_x far from the study cities (outside the 12-km domain) that is transformed to nitrate prior to reaching the city. In January 2000, CHI had the highest predicted nitrate concentration of 4.80 μg m^{-3}, followed by BAL, NYC, and DET with concentrations close to 4 μg m^{-3}. W-S had
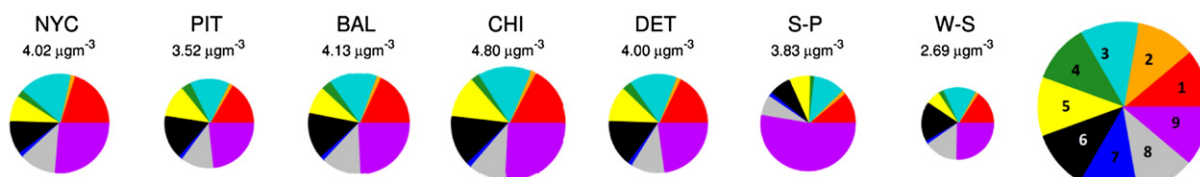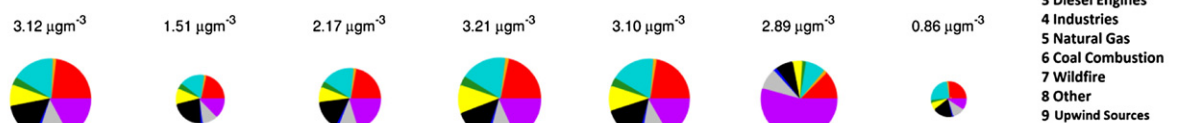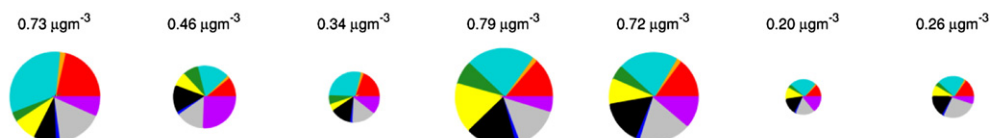
Fig. 5. Source apportionment of January and August PM$_{2.5}$ nitrate for the seven cities.

the lowest predicted nitrate concentration of 2.69 μg m^{-3}, with concentrations at S-P and PIT predicted to be between 3–4 μg m^{-3}. On-road gasoline vehicles and diesel engines account for similar portions of nitrate concentrations (approximately 15–20% each) at all cities. Natural gas and coal combustion each contribute approximately 10–15% to nitrate concentrations. All other local sources together account for approximately 25% of total nitrate. Off-road gasoline engines and other industrial sources account for a very small fraction of total nitrate. Nitrate formed from upwind sources exceeds any single local source category, and accounts for 20–25% of total nitrate at all cities except S-P where it accounts for more than 50%. S-P is very close to the west boundary of the 12-km domain and thus has highest upwind contributions. These results suggest that emission reduction programs at the national scale would be effective at reducing particulate nitrate pollution in individual cities.

The second row of Fig. 5 shows the nitrate concentration and source apportionment results for January 2006. Overall nitrate concentrations at all cities decrease by more than 20% compared to 2000, with the largest reduction of 68% predicted at W-S. Although the absolute contributions from local sources also decrease significantly, percentage contributions from local sources to total nitrate increase due to a significant decrease of contributions from upwind sources at all cities except for S-P. A more detailed analysis of the changes in the upwind vs. local source contributions is presented in Section 4.3.

The total concentration of nitrate is much lower in August compared with January (the third and fourth rows of Fig. 5) because hotter temperatures favor the partitioning of nitrate to the gas phase. The maximum August predicted nitrate concentration in 2000 among the seven cities was 0.79 μg m^{-3} at CHI, slightly higher than NYC and DET. Nitrate concentrations at other cities are much lower. Diesel engines are the dominating source for summer nitrate concentrations at all cities with

a maximum relative contribution of 30% at NYC. Other significant summer nitrate sources include on-road gasoline, natural gas, and coal combustion. Unresolved sources that were not individually tracked in the source apportionment calculations also play an important role in August with a contribution of 15–20% at all cities. Upwind sources account for less than 20% in all cities except PIT.

A comparison between results for August 2000 and 2006 shows decreased nitrate concentrations at all cities except DET and S-P. Predicted nitrate concentrations at NYC experienced the largest decrease, from 0.73 to 0.27 μg m^{-3}, followed by CHI, from 0.79 to 0.50 μg m^{-3}. Decreased contributions from diesel engines, natural gas and coal combustion account for the majority of the reductions. Contributions from upwind sources to nitrate in DET and S-P increase slightly, resulting in a slight increase of August nitrate concentrations from 2000 to 2006. This trend is likely caused by different meteorological patterns in August 2000 vs. 2006 since national emissions of NO$_x$ decreased over this time period.

First two rows of Fig. 6 shows the predicted January and August sulfate concentrations and source contributions for the seven target cities in 2000 and 2006. In 2000, January sulfate concentrations at all cities range from 2.48 (W-S) to 3.90 μg m^{-3} (S-P) (the first row of Fig. 6). Contributions due to upwind sources are higher than any single local source at all cities, accounting for more than 50% of total sulfate except for S-P. Coal combustion is the largest local source followed by other unresolved sources. Natural gas and industries also account for a significant portion of the sulfate in S-P. January sulfate concentrations at all cities except NYC decrease from 2000 to 2006. The maximum decrease of 2.28 μg m^{-3} occurs at S-P, where contributions from coal combustion and industries are decreased the most. The overall decrease of sulfate concentration is due to large decrease of SO$_2$ emissions from sources other than coal combustion. Contributions of coal combustion to
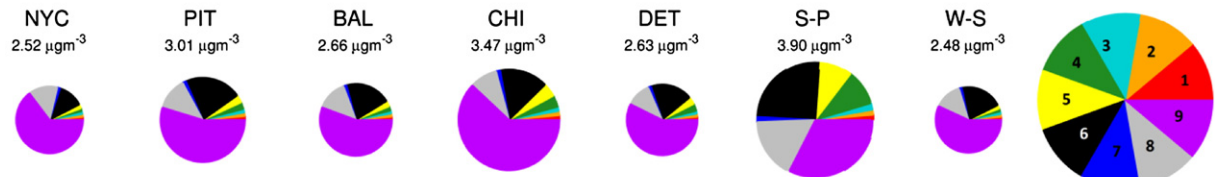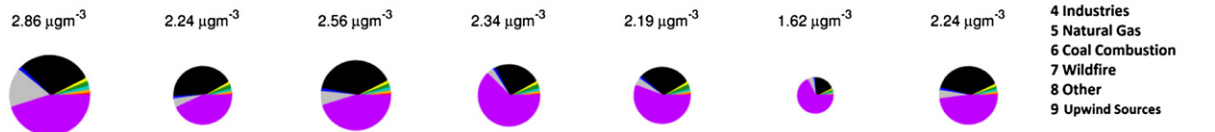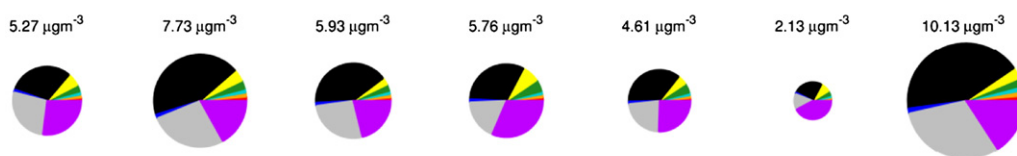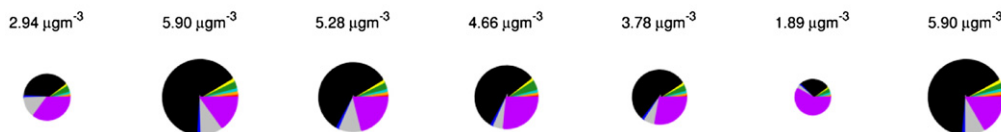
Fig. 6. Source apportionment of January and August PM$_{2.5}$ sulfate for the seven cities.

absolute January sulfate concentrations for all other cities increase by 10% (CHI) to 180% (NYC). Upwind sources still contribute more than any single local sources at all cities.

The third and fourth rows of Fig. 6 show that predicted August sulfate concentrations are generally higher than January concentrations for both 2000 and 2006. Higher concentrations of sulfate in August are expected because of faster photochemical transformation of SO$_2$ into sulfate in summer conditions. In 2000, the maximum predicted August sulfate concentration is at W-S (10.13 μg m^{-3}). Coal combustion is the

dominating source followed by other unresolved sources and upwind contributions at all cities except S-P which is dominated by the upwind sources. Natural gas and industrial sources also contribute to 10–15% of total predicted sulfate. Predicted August sulfate concentrations decrease between 2000 and 2006, especially at NYC and W-S, as shown in the fourth row of Fig. 6. The relative contribution from coal combustion increases at all cities except S-P because of a significant decrease of the relative contributions from unresolved sources to SO$_2$ emissions in 2006. The SO$_2$ emissions from unresolved sources account for 13.6% of
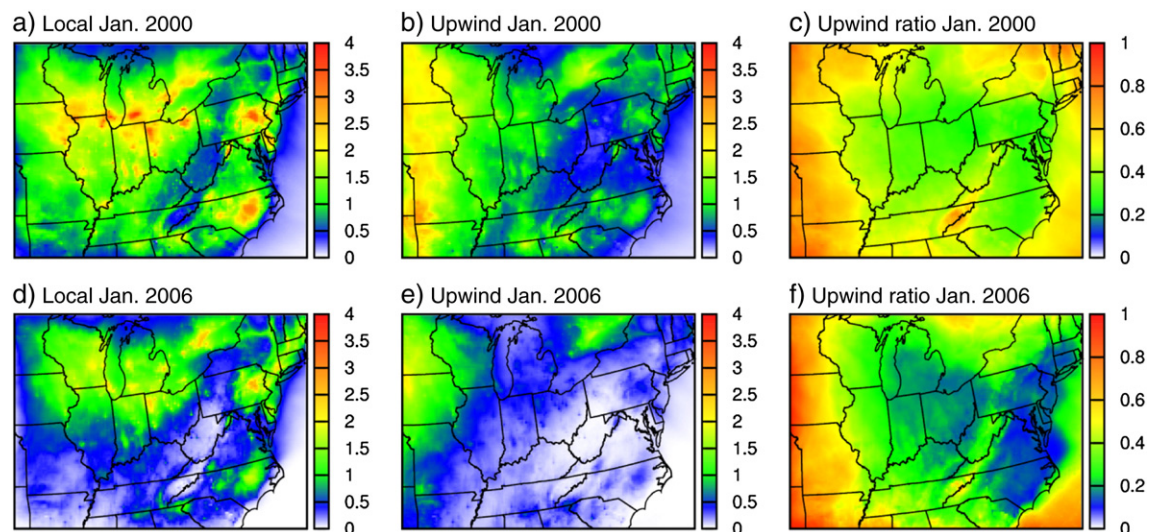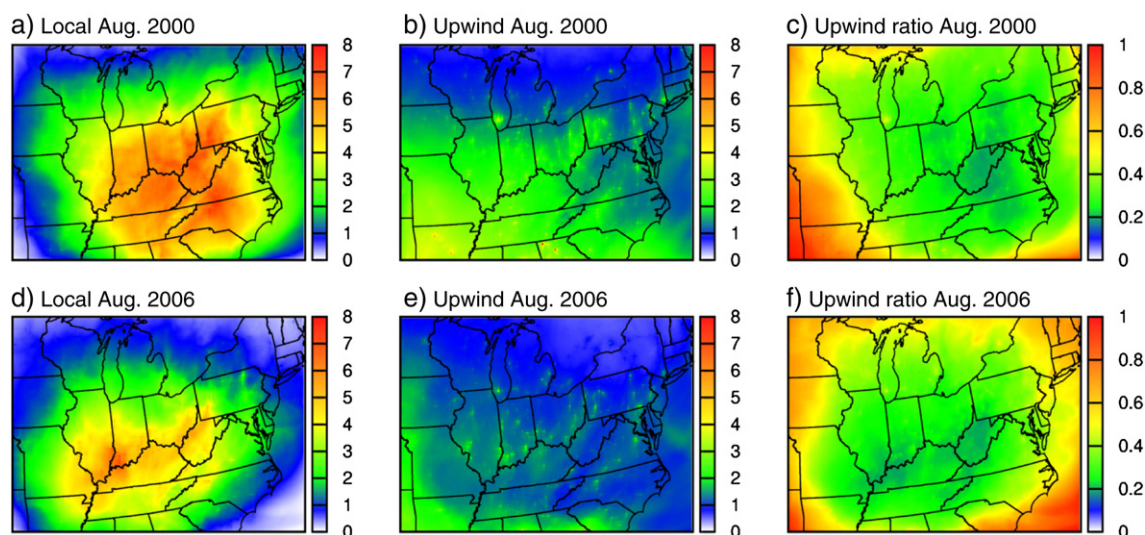

Fig. 7. Regional contributions of local and upwind sources to January PM$_{2.5}$ nitrate within the 12-km eastern US domain in 2000 and 2006. Units for panels (a), (b), (d), and (e) are μg m^{-3}.

Fig. 8. Regional contributions of local and upwind sources to August PM$_{2.5}$ sulfate within the 12-km eastern US domain in 2000 and 2006. Units for panels (a), (b), (d), and (e) are μg m^{-3}.

the total SO$_2$ in 2000 August, but decrease to 10.0% in 2006 August (as shown in Table 1). Accordingly, relative contributions from natural gas, other unresolved sources and upwind sources all decrease.

4.3. Local vs. upwind contributions

As discussed in Section 3.2, upwind sources outside the 12-km domains can contribute significantly to total nitrate and sulfate concentrations at the target cities in the current study. Fig. 7 shows the contributions of local and upwind sources to January nitrate in the 12-km domain for 2000 and 2006. High nitrate concentrations due to local sources (3–4 μg m^{-3}) occur in the Midwest states, Pennsylvania, and North Carolina (see Fig. 7(a)). Upwind nitrate enters the domain mainly from the west boundary with a maximum concentration of approximately 3 μg m^{-3}. Absolute contributions of upwind sources decrease to approximately 1 μg m^{-3} and below in other portions of the 12 km domain. As shown in Fig. 7(c), upwind sources account for more than 50% of nitrate concentrations close to west boundary and more than 20% in the central portion of the domain. Nitrate concentrations associated with local sources within the 12-km domain decreased by approximately 1 μg m^{-3} between January 2000 and 2006 (Fig. 7(d)) but the relative spatial pattern of local source contributions is similar for the two comparison years. Upwind source contributions to nitrate decreases to less than 0.5 μg m^{-3} in the most portions of the 12 km domain. The relative importance of upwind sources is significantly reduced across the majority of the domain, with a slight increase in relative importance near the western boundary (Fig. 7(f)). In the east coast and Midwest states, the contribution of upwind sources to nitrate decreases to less than 20% in January 2006. As noted previously, this trend may be caused by different meteorology in January 2000 and 2006. However, the detailed cause of this reduction in upwind contributions needs further investigation.

As shown in Fig. 8(a), sulfate has a much broader regional distribution than nitrate, and high concentrations of sulfate from local sources occur in the middle of the domain with a maximum concentration of 8 μg m^{-3} in August 2000. PIT, BAL, and W-S are within the region with the highest concentrations, while NYC, CHI, and DET are near the edge of the high concentrations region. Fig. 8(b) shows that upwind sources contribute approximately 2–3 μg m^{-3} of sulfate in general. Areas near the south and southeast boundary of the domain have much higher relative contributions from upwind sources. The upwind contribution to total sulfate is approximately 30–40% in the most areas of the 12-km domain and up to 80–100% near boundaries, especially on the southwest, as shown in Fig. 8(c). Fig. 8(d) and (e) shows that there is a significant decrease of both the local and upwind sulfate

concentrations from 2000 to 2006. The area where peak local concentrations occur shifts slightly westward. The upwind contribution decreases to 1–2 μg m^{-3} in the inner areas of the domain. Although the concentrations decrease, the relative contributions of upwind to total sulfate do not change significantly and there is a slight increase near the east boundary.

Since the 12-km domain covers most areas in the eastern US, the upwind contributions are mostly from regional transport but some of them might be the recirculation of emissions from the 12-km domain. A separate study is needed to quantitatively determine the source region origin of the upwind sources by tagging the emissions from different source regions. Wind direction and speed affect the amount of contributions from the upwind sources but the contributions are also affected by other meteorological conditions such as temperature and solar radiation, which affect the formation of secondary inorganic aerosol components. Lower temperature and less solar radiation in winter allow precursors NO$_x$ and SO$_2$ from upwind sources to travel further into the domains to compete with local emissions. In summer time, precursors enter the domain are transformed into particulate matter and thus more easily removed from the atmosphere, and thus have less contribution to the total concentrations at receptor sites inside the domains.

4.4. Impact of emissions reductions

Simulations were performed using the 2000 meteorology and 2006 emissions to separate the effects of emission reductions vs. changes to meteorology on predicted nitrate and sulfate concentrations. Regional differences in monthly-average nitrate and sulfate between two simulations using 2000 and 2006 meteorology (both with 2006 emissions) are shown in Fig. 9 (a–d) to show the effect of difference in meteorology conditions on predicted nitrate and sulfate concentrations. Regional differences of monthly average nitrate and sulfate between simulations using 2006 emission and 2000 meteorology and simulations using 2000 emission and 2000 meteorology are shown in Fig. 9(e–h). These differences indicate the roles of emissions reduction in nitrate and sulfate concentrations.
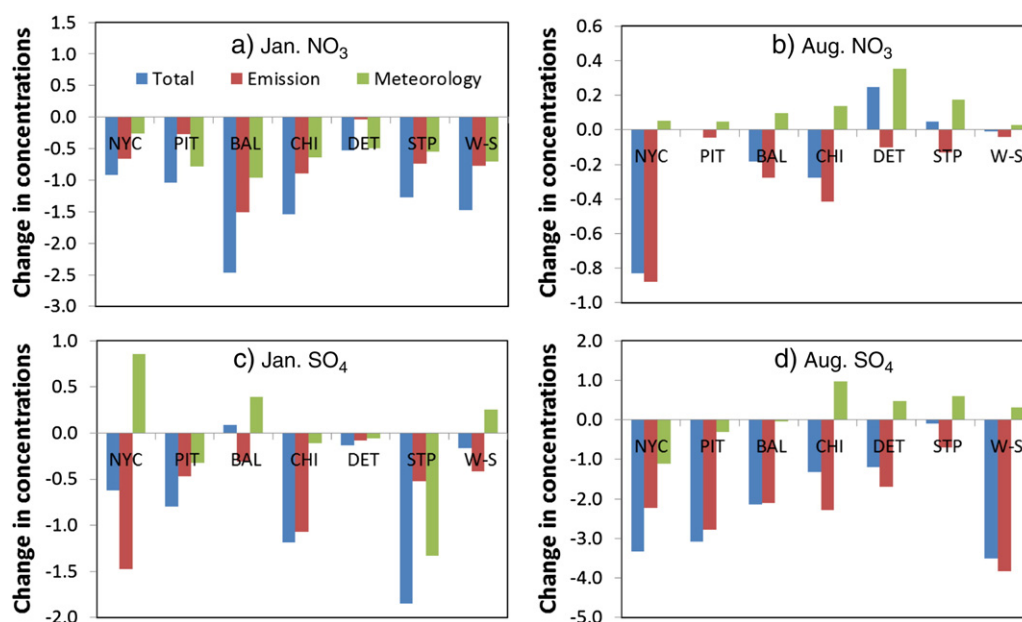
Fig. 10 shows the overall differences (calculated by the concentrations using 2006 meteorology and emissions minus those using 2000 meteorology and emissions) in predicted nitrate and sulfate concentrations, and the changes due to emission reduction (calculated by the concentrations predicted using 2000 meteorology and 2006 emissions minus those using 2000 meteorology and emissions) and meteorology variations (calculated by the concentrations predicted using 2000 meteorology and 2006 emissions minus those using 2006 meteorology and
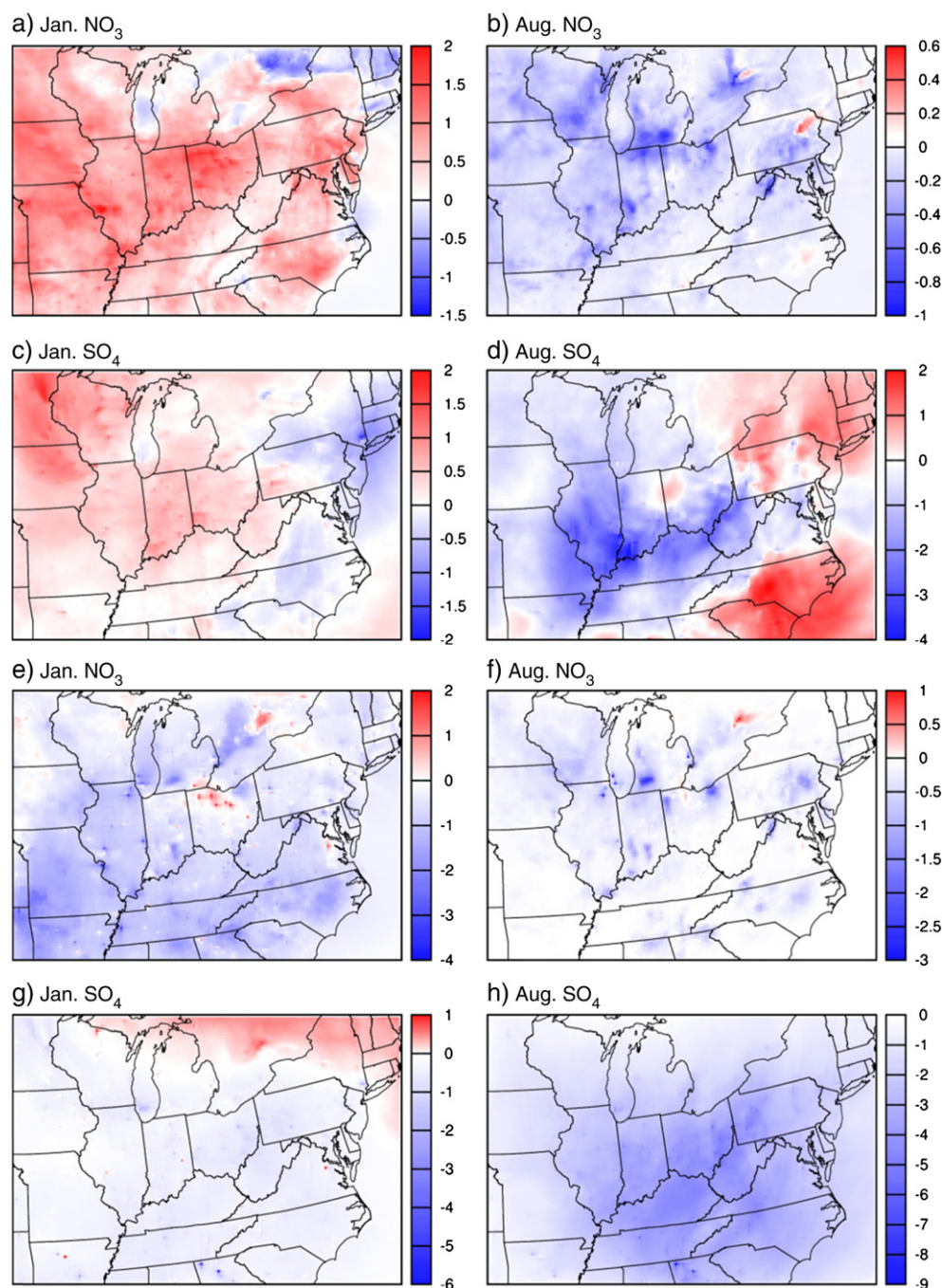
Fig. 9. Regional differences in monthly-average PM$_{2.5}$ nitrate and sulfate due to meteorology differences (a–d) and emission differences (e–h) within the 12-km domain. For panels (a)–(d), the differences are calculated by the concentrations using 2000 meteorology and 2006 emissions minus those using 2006 meteorology and emissions. For panels (e)–(h), the differences are calculated by the monthly-average concentrations using 2000 meteorology and 2006 emissions minus those using 2000 meteorology and emissions. Units are μg m^{-3}.

emissions) for the seven cities. In January both emissions and meteorology contribute to the reduction of nitrate in all cities from 2000 to 2006. On average, emission control accounts for 47% of the total concentration reduction (from the lowest reduction of 8% in DET to the highest reduction of 72% in NYC) and the remaining 53% of the concentration reduction is due to meteorology variations. For August nitrate, there is a net decrease in NYC, BAL, and CHI, a net increase in DET and S-P, and nearly no changes in PIT and W-S from 2000 to 2006. Averaged over the seven cities, the net decrease of nitrate is approximately 36%. Emission controls alone would lead to an average decrease of nitrate by approximately 69% but it is offset by increases associated with meteorological conditions that favor nitrate formation. As shown in Fig. 10(c), January sulfate concentrations at the seven cities all decrease from 2000 to

2006 except at BAL. Meteorology variations lead to a decrease in predicted sulfate concentrations in PIT, CHI, DET, and S-P but cause an increase in NYC, BAL, and W-S. Averaged contributions of emission controls and meteorology variations to the net reduction are 93% and 7%, respectively. As shown in Fig. 10(d), August sulfate concentrations at all cities decreased from 2000 to 2006 but at CHI, DET, S-P and W-S the concentration reduction is offset by approximately 6% on average due to meteorology. In general, that apparent effectiveness of emissions control programs for nitrate is increased by meteorology conditions that are less favorable for nitrate formation in 2006 vs. 2000. The apparent effectiveness for control programs for January sulfate, August nitrate and sulfate is decreased by more favorable meteorological conditions in 2006 for the formation of these pollutants. These results emphasize

Fig. 10. Overall differences in predicted nitrate and sulfate concentrations and the contributions to the overall changes due to emission reductions and meteorology variations for the seven cities. Note these concentrations are based on the 12-km domain results. Units are μg m^{-3}.

the importance of separately accounting for the effects of meteorology and emissions during accountability studies for control programs.

Analysis of the surface meteorology conditions between August 2000 and 2006 shows that for August 2006 there is a significant increase in relative humidity by 10–30% in the southern part of the domain and a decrease of wind speed by 0.5–1.5 m s^{-1} throughout the domain. Increasing RH can lead to higher OH concentrations in the gas phase which enhance gas phase oxidation of SO$_2$ and NO$_x$ and may also increase sulfate formation through the aqueous oxidation pathways. Reduced wind speed can lead to less dilution and thus higher nitrate and sulfate concentrations as well. For January 2006, the average surface wind speed is significantly higher than that of January 2000 by 2 m s^{-1}, which may lead to lower concentrations of both nitrate and sulfate. The monthly-average temperature is also significantly higher than that of January 2000 by 5 to 9 K throughout the land part of the domain, which shifts the partitioning of nitrate toward gas phase. These two factors explain the predicted higher nitrate and sulfate when using January 2000 meteorology with 2006 emissions.

The accuracy of the predicted secondary PM concentrations and source apportionment results in this study are affected by several factors such as emissions and meteorology, as well as model formulations. In general, the uncertainties in the meteorology and model formulations are likely going to affect predictions of aerosol formation from all sources so the relative contributions of different sources are unaffected. However, uncertainty in the emissions can affect both absolute concentrations and relative contributions. Analyses of the differences between different modeling scenarios are likely less affected by these uncertainties in model formation and input as the uncertainties are expected to be canceled out mostly.

5. Conclusions

In this study, the concentrations of winter (January) and summer (August) secondary inorganic PM components (nitrate and sulfate) and contributions from major sources for the 7 cities in the eastern US are determined for the years 2000 and 2006 using a source-oriented version of CMAQ. Generally, total nitrate and sulfate concentrations decrease from 2000 to 2006 for most of the cities. January nitrate concentrations decrease by 25–68% for all the cities while August nitrate concentrations decrease for 5 out of 7 cities by a maximum of 68% in

NYC while DET and S-P experience increasing concentrations by up to 33%. Major local nitrate sources include highway gasoline vehicles, diesel engines, natural gas and coal combustion. January sulfate concentrations decrease from 2000 to 2006 in all cities by 4–58% except NYC, which increases by 13%. August sulfate concentrations decrease by 11–44% in all cities. Coal combustion and natural gas are the dominating local sources for sulfate. Upwind emissions of nitrate and sulfate precursors play significant roles in January nitrate and August sulfate formations. In the interior of the 12-km eastern US domain, the contribution of upwind sources to nitrate reduced from 20–40% to 10–20% from 2000 to 2006 while the contribution to sulfate remains at approximately 50%. Considering the importance of upwind sources, regional joint emission control strategies would be necessary for PM$_{2.5}$ control in the eastern US. On average, approximately 53% of the reduction in nitrate and 93% of the reduction in sulfate between January 2000 vs. 2006 are driven by emission controls, with the remaining change due to meteorological variations. In August, emission controls actually lead higher reduction in nitrate and sulfate than the apparent differences between 2000 and 2006 results but the effects were offset by meteorology variations by 33% and 6%, respectively. This implies that the variability in regional weather must be considered during accountability studies that evaluate the effectiveness of short term emission control programs for these secondary inorganic pollutants. In this study, it also shows that "upwind sources" is very important for air quality improvement and future studies are needed to elaborate their source and geographical origins.

Conflict of interest

Acknowledgment

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